Involvement of a Binuclear Species with the Re-C(O)O-Re Moiety in CO_2 Reduction Catalyzed by Tricarbonyl Rhenium(I) Complexes with Diimine Ligands: Strikingly Slow Formation of the Re-Re and Re-C(O)O-Re Species from $Re(dmb)(CO)_3S$ (dmb = 4,4′-dimethyl-2,2′-bipyridine, S = Solvent)

Yukiko Hayashi, Shouichi Kita,[†] Bruce S. Brunschwig, and Etsuko Fujita*

Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000
E-mail fujita@bnl.gov

Supplementary Materials

Table S1. Reduction potentials (vs SCE) of Re complexes using a glassy carbon electrode in CH_3CN solutions containing 0.1 N Bu_4NPF_6 at a scan rate of 100 mV s^{-1}

Complexes	$E_{1/2}$, V vs SCE		
$Re(bpy)(CO)_3Cl$	1.42,[a]	-1.37,	-1.78[b]
$Re(bpy)(CO)_3Br$	1.39,[a]	-1.37,[c]	-1.64[b]
$Re(bpy)(CO)_3(CH_3CN)(PF_6)$	1.80,	-1.24,	-1.46[b]
$Re(bpy)(CO)_3(O_2CH)$	1.35,	-1.34,	-1.75[b]
$Re(bpy)(CO)_3(NO_2)$	1.48,[a]	-1.32,	-1.76[b]
$Re(bpy)(CO)_2(P(OEt)_3)_2PF_6$	1.44,[c]	-1.38,	-2.01[b]
$[Re(bpy)(CO)_3]_2$	-0.07,[a]		
$[Re(bpy)(CO)_3]_2$[d]	-0.10,[a]		
$Re(dmb)(CO)_3Et$	0.71,[a]	-1.61,	-2.26[b]
$Re(dmb)(CO)_3H$	0.09,[a]	-1.58,[c]	-2.27[b]
$Re(dmb)(CO)_3(O_2CH)$	1.33,	-1.43,	-1.83[b]
$Re(dmb)(CO)_3(CH_3CN)(PF_6)$	1.76,	-1.32,	-1.50[b]
$Re(dmb)(CO)_3Cl$	1.38,[a]	-1.47,[c]	-1.80[b]
$Re(dmb)(CO)_3Br$	1.36,[a]	-1.46,[c]	-1.68[b]
$Re(dmb)(CO)_3(OH)$	1.34,[a]	-1.51,[c]	-2.01[b]
$Re(dmb)(CO)_3(P(OEt)_3)PF_6$	1.78,[c]	-1.34,	-1.80[b]
$Re(dmb)(CO)_3(SO_3CF_3)$[d]	1.77,	-1.32,	-1.49[b]
$[Re(dmb)(CO)_3]_2$	-0.16,[a]		

[a] E_{pa}, [b] E_{pc}, [c] quasi-reversible, [d] in 1,2-difluorobenzene at a scan rate of 200 mV s^{-1}, O'Toole, T. R.; Younathan, J. N.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem*., **1989**, *28*, 3923-3926. [d] The redox potentials of this complex is similar to those of $Re(dmb)(CO)_3(CH_3CN)(PF_6)$ indicating that triflate ion is not coordination in acetonitrile. It is reported that $Re(bpy)(CO)_3(SO_3CF_3)$ dissolves with ionization in acetonitrile. See Sullivan, P; Meyer, T. J. *J. Chem. Soc., Chem. Commun*. **1984**, 1244-1245

Figure S1. UV-vis spectra of $Re(dmb)(CO)_3(OTf)$ (red), $[Re(dmb)(CO)_3]_2$ (green) and $[Re(dmb)(CO)_3]^-$ (purple) in THF

Figure S2. UV-vis spectra of $[Re(dmb)(CO)_3]_2$ in various solvents: THF (black), acetone (green), and CH_3CN (red).

Figure S3 Plot of observed pseudo-first-order rate constant vs CO_2 concentration for decomposition of $[Re(dmb)(CO)_3]_2(CO_2)$ at 25 °C in DMF

Figure S4 Plot of observed pseudo-first-order rate constant vs CO_2 concentration for decomposition of $[Re(dmb)(CO)_3]_2(CO_2)$ at 25 °C in DMF under continuous irradiation.

Figure S5 Decay and formation of species in the reaction of $Re(dmb)(CO)_3(COOH)$ in DMF: $Re(dmb)(CO)_3(COOH)$, ■ $[Re(dmb)(CO)_3]_2(CO_2)$, ▼ $Re(dmb)(CO)_3(OC(O)OH)$, ● H_2O.

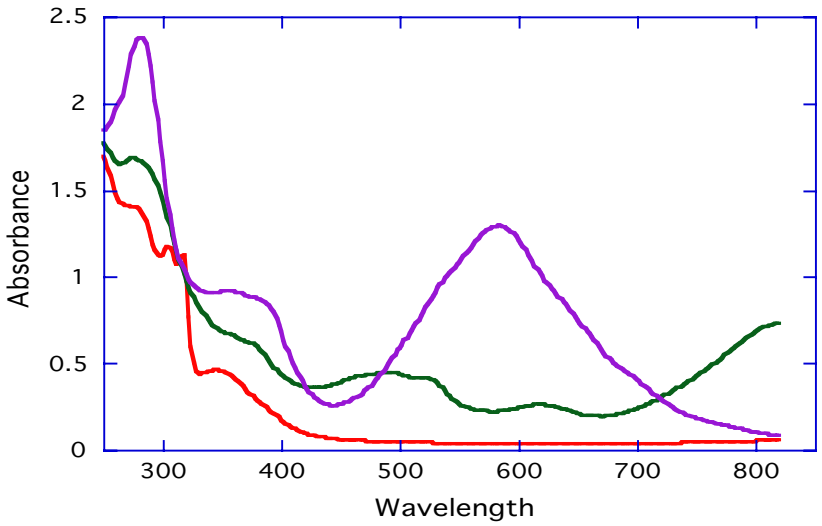

Figure S1.

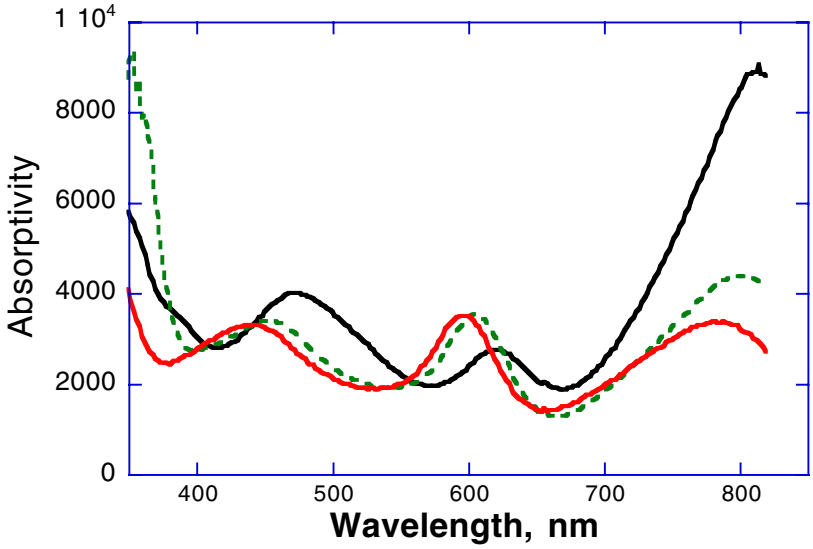
1 10^4
8000
6000
4000
2000
0
Absorptivity
400
500
600
700
800
Wavelength, nm

Figure S2.

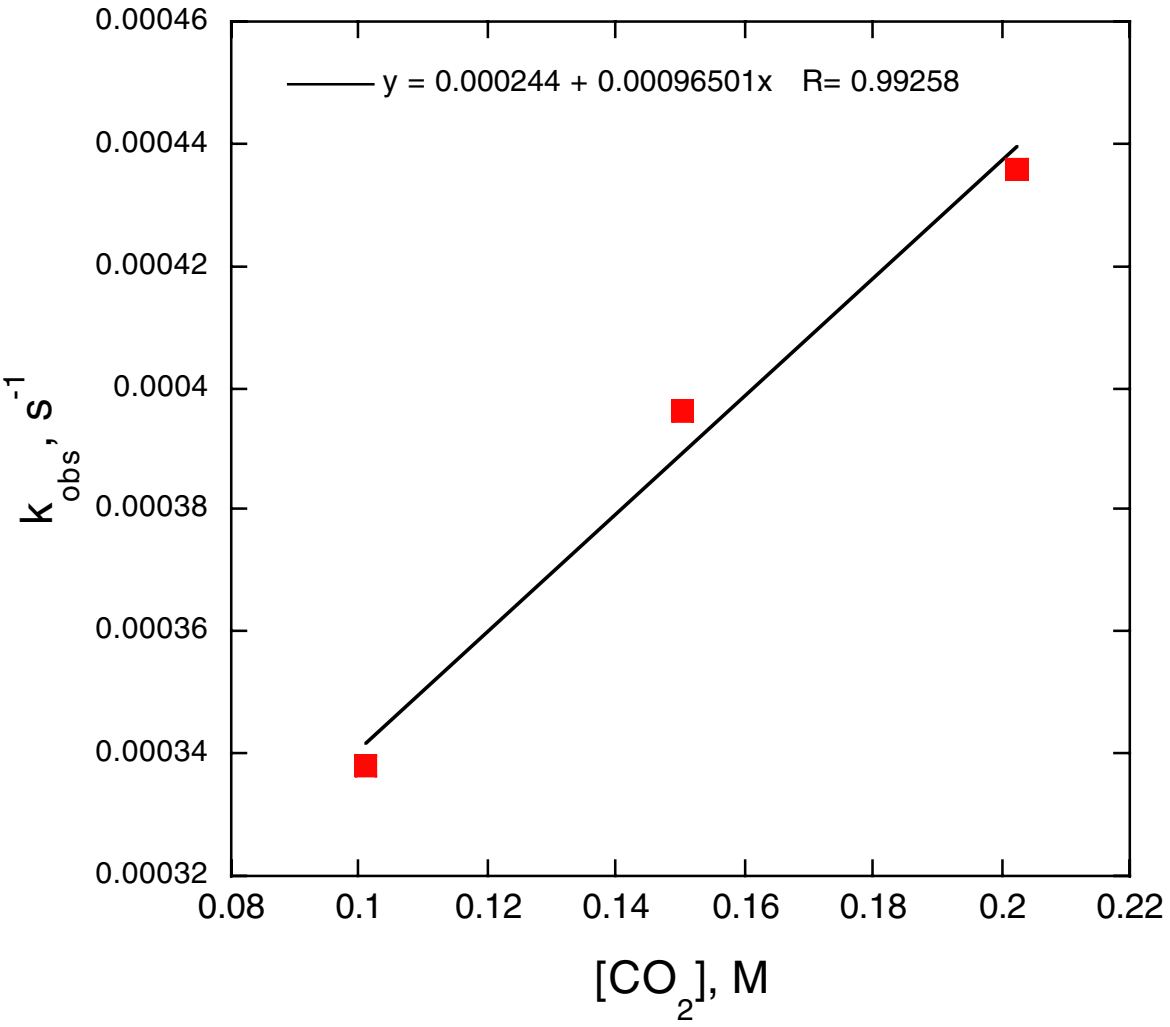
y = 0.000244 + 0.00096501x R= 0.99258
0.00046
0.00044
0.00042
0.0004
0.00038
0.00036
0.00034
0.00032
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
k obs, s-1
[CO2], M

Figure S3.

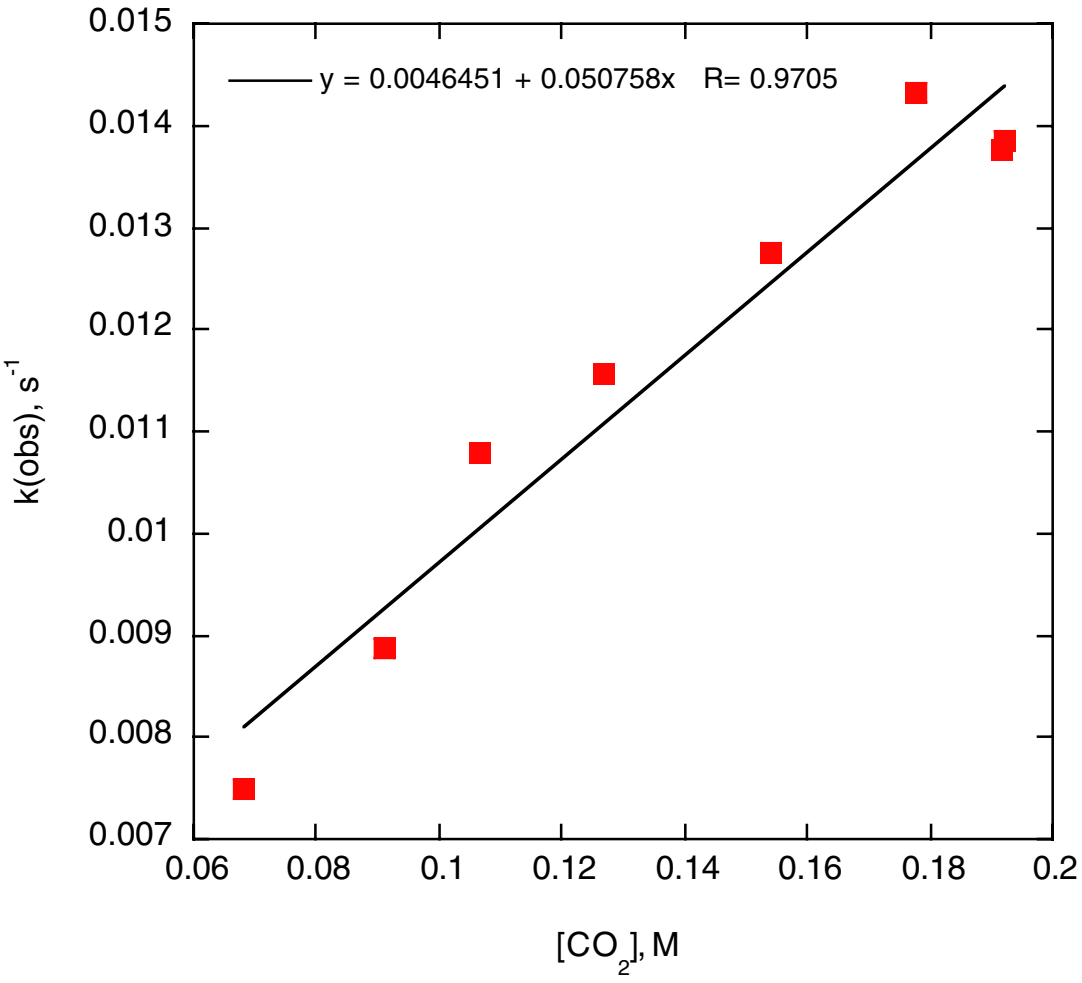
y = 0.0046451 + 0.050758x R= 0.9705
k(obs), s-1
[CO2], M
0.015
0.014
0.013
0.012
0.011
0.01
0.009
0.008
0.007
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2

Figure S4.

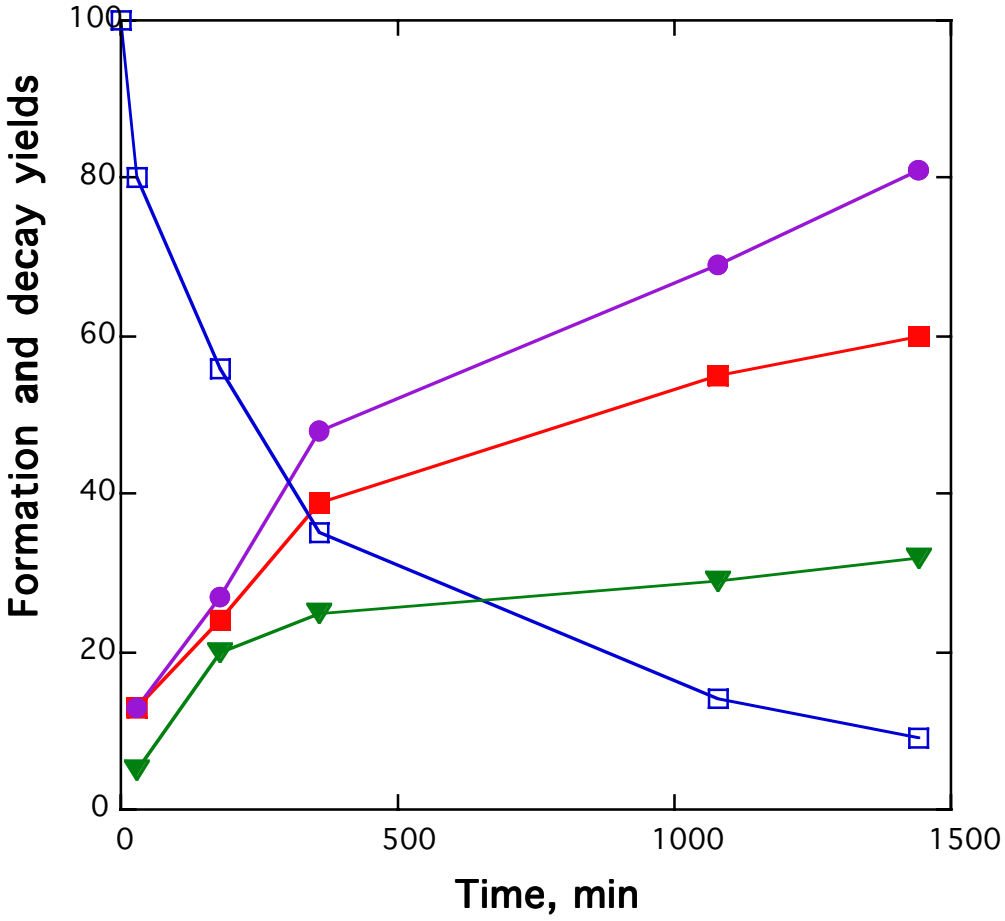
Formation and decay yields
Time, min
0
20
40
60
80
100
0
500
1000
1500

Figure S5